HIT-170

THERMOELECTRIC BONDING STUDY

Covering the Period from
1 March through 31 May 1965

June 30, 1965

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NASA Contract NAS5-3973

Prepared for
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Goddard Space Flight Center

HITTMAN ASSOCIATES, INC.
BALTIMORE, MARYLAND

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THERMOELECTRIC BONDING STUDY

Quarterly Progress Report
For the Period
1 March through 31 May 1965

I. INTRODUCTION

Since its inception this program has been concerned with obtaining an understanding of the process by which lead telluride thermoelectric elements may be bonded to metal contacts or shoes and of the mechanisms by which bonds fail or degrade. A satisfactory bond must have minimum electrical and thermal resistance and adequate strength. These properties must be maintained throughout the operating lifetime of the element without excessive degradation. Further, any shoe or braze material used should have the smallest possible deleterious effects on the performance of the thermoelectric material itself.

During the first phase a systematic approach was applied to the selection of braze and shoe materials for use with n- and p-type PbTe thermoelements. The two principal causes of bond degradation were poisoning resulting from diffusion and thermal stresses resulting from expansion mismatch between the element and shoe. Of the braze alloys investigated only SnTe and titanium modified SnTe formed satisfactory bonds with minimal degradation to lead telluride. Several shoe materials appeared useful and iron was chosen for continued study on the basis of its general use in this application (Reference 1).

The objectives of the current phase of this program are to optimize the bonding procedure for joining lead telluride to iron with a modified or unmodified tin telluride braze, to extend the bonding process to p-PbSnTe material, and to carry out long term tests on bonded and unbonded PbTe thermoelements. The tests will be used to increase our understanding of the mechanisms involved in bond degradation. Specimens, with known properties will be tested under operating conditions for periods of time from 100 to 5000 hours. Properties will be monitored during the test period. Samples removed from test will be evaluated electrically and metallographically. Electron probe microanalysis will be performed on selected samples in cooperation with NASA-GSFC.

Progress to date in these areas is reported in the following sections.

Reference 1. Thermoelectric Bonding Study - Summary Report, Report HIT-163 prepared under Contract NAS5-3973 (1965)

II. DESIGN AND CONSTRUCTION OF THE THERMOELECTRIC ELEMENT TEST APPARATUS

The testing device being built for this program was designed with several important requirements. These are enumerated below:

1. Individual PbTe thermoelectric elements, rather than couples or modules, are to be tested.

2. Parameters to be measured include hot junction temperature, cold junction temperature, output voltage, power output and element resistance.

3. All measurements are to be made remotely without disturbing the elements on test.

4. All elements will be tested under inert atmosphere (argon).

5. Isolation will be provided for groups of specimens.

6. Provision has been made for replacement of failed elements with minimum disruption of testing.

7. Materials of construction have been chosen so as to assure no contamination of the thermoelectric elements.

The device that resulted from these requirements consists of four individual water cooled chambers, each capable of holding six thermoelectric elements. Each chamber, one of which is pictured in Figure 1, has its own water and argon supply, an individually controlled heater block, and a low resistance junction box immediately adjacent. Each element under test is connected to a pair of terminals at this junction box. By connecting a set of portable meters to each pair of terminals direct readings of voltage and resistance will be made for each element in turn. From this the output power can be calculated.

Thermocouples at the hot and cold junction of each thermoelectric element will be connected to a patch panel at the control console shown in Figure 2. At this point each temperature can be read with a millivolt potentiometer or can be recorded on a twelve point Honeywell recorder.

This console also contains the controllers for the heater block temperature. Provision has been made to cut off power in case of loss of water cooling or if the heater block thermocouple fails. An extra thermocouple will be installed in each heater block. This thermocouple can be connected to the controller by switching leads at the control console. Thus it will not be necessary to open the inert atmosphere test chambers in the event of a thermocouple failure.

Construction of this test system is well underway and completion is scheduled for the first week in July.

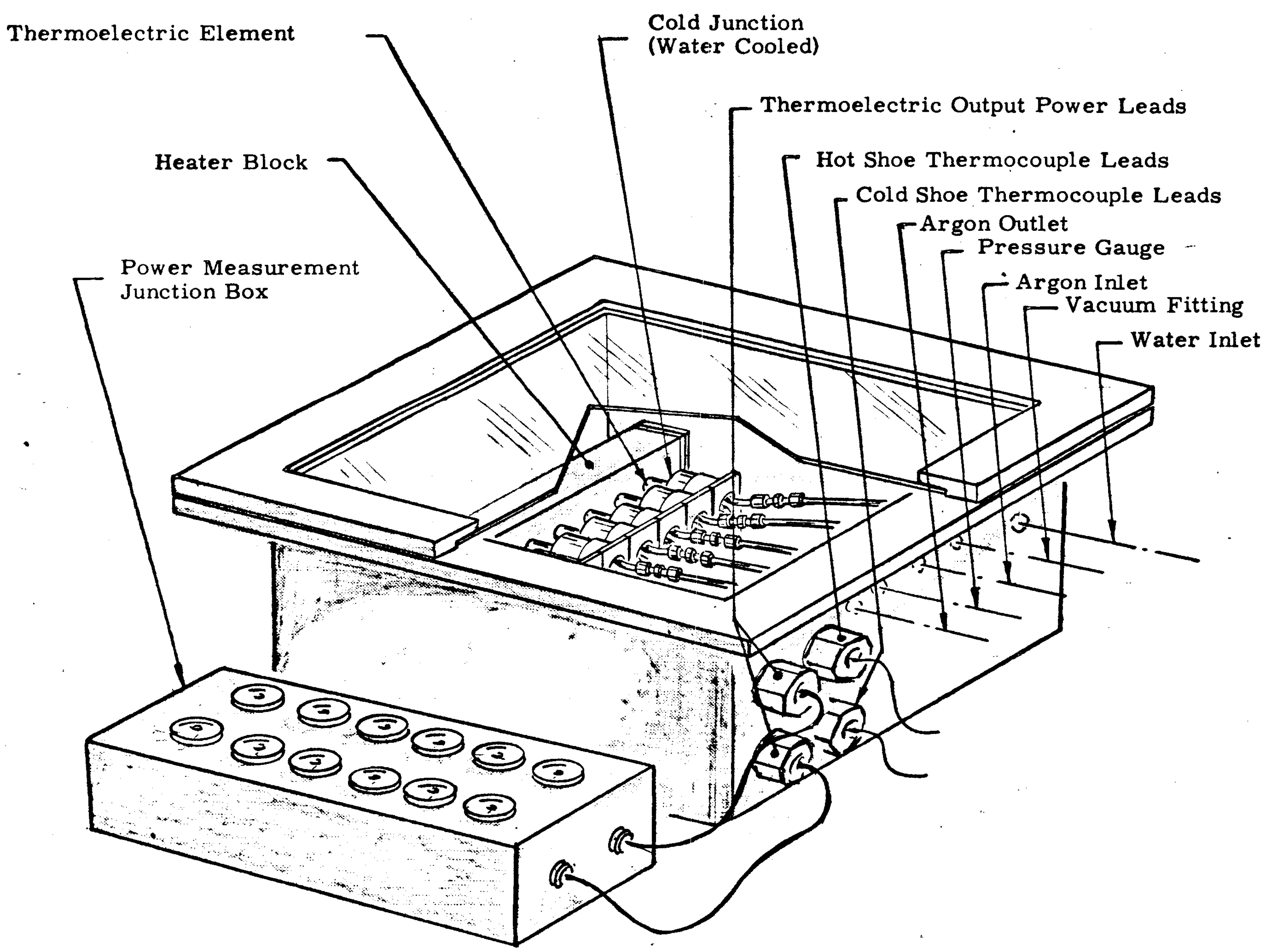

Figure 1. Thermoelectric Test Unit

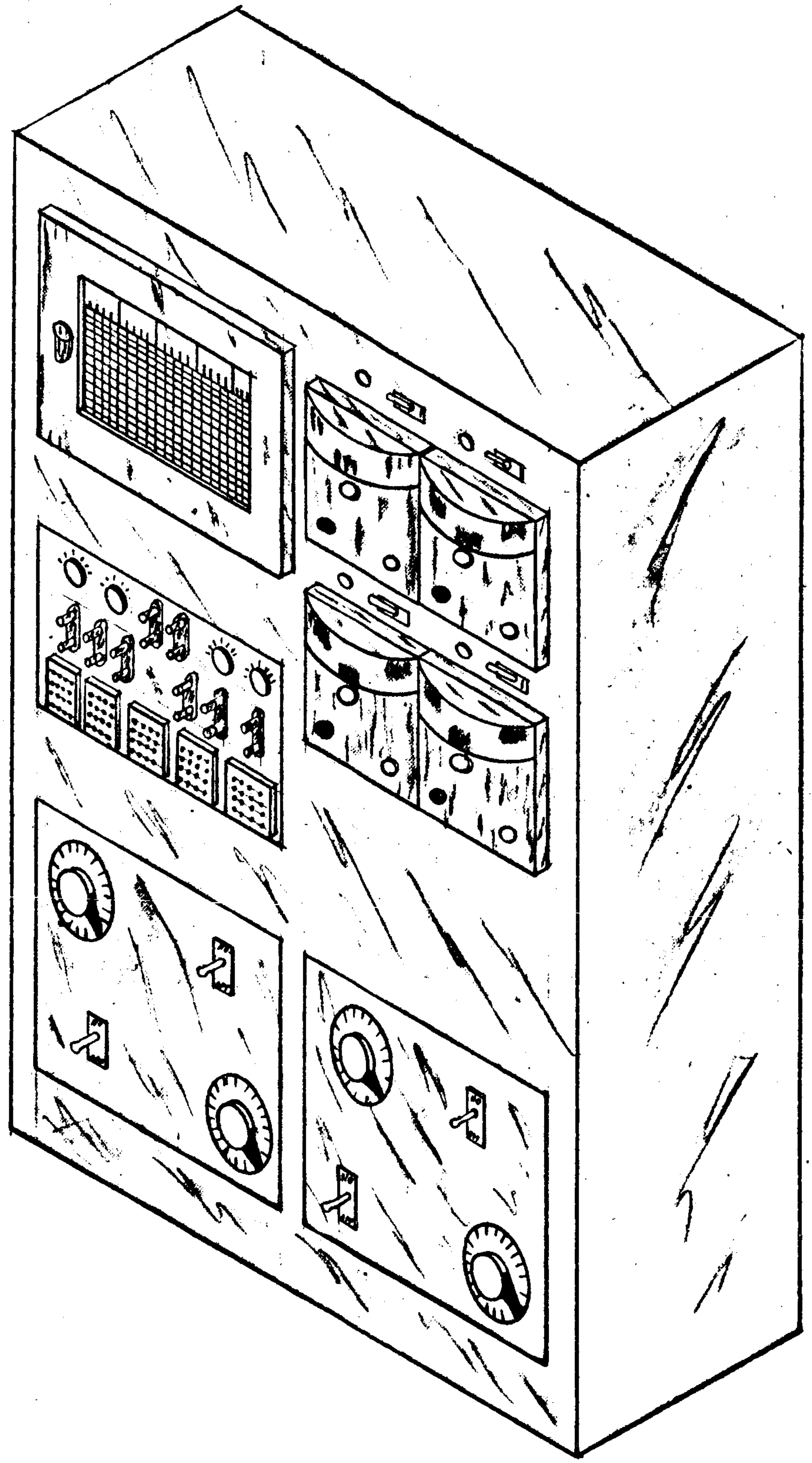

Figure 2

Thermoelectric Element Tester Control Console

III. FABRICATION OF THERMOELECTRIC ELEMENTS

All thermoelectric elements used in this program, except for controls, are fabricated at Hittman Associates from powders purchased from 3M. The release test data provided by 3M on the material supplied is as follows. Each value is based on three samples pressed by the vendor from each batch.

n-PbTe	Lot 942-B-1	$\rho = 195$ $\mu\Omega$-in.	emf (Δ T = 600°F) = 63 mv
p-PbSnTe	Lot 943-B-1	$\rho = 353$ $\mu\Omega$-in.	emf (Δ T = 800°F) = 68 mv

These values were compared with 3M's published property data. The vendor states that materials provided by them will have properties within $\pm$ 10 percent of the published values. On this basis neither lot would be acceptable. The n-PbTe should have an emf of 72 $\pm$ 7 mv for a Δ T of 600°F, and the p-PbSnTe resistivity should be 402 $\pm$ 40 $\mu\Omega$ -in. Since, in each case, the deviation from acceptable limits was small it was decided to use the powders in our program.

A hot pressing fabrication process for PbSnTe elements was developed. The procedure employed earlier for p-PbTe was not satisfactory and it was necessary to increase temperature and load to obtain sound bodies of p-PbSnTe. It was found that high density, relatively strong elements, 3/8 inch diameter by 3/4 inch long could be consistently hot pressed in the following manner:

The proper quantity of -200 mesh powder was weighed out and placed in a graphite die. The ends of the die pins were coated with high purity alumina to prevent sticking to the compact. The die assembly was placed in an argon atmosphere chamber, purged, heated rapidly by induction to 816°C (1500°F), loaded to 1.5 tsi, held for five minutes and allowed to cool to $\sim$150°C under load.

Approximately one hundred PbSnTe thermoelements have been produced by the above process during this quarter. In addition several n-PbTe elements were manufactured by the above or similar processes.

Room temperature electrical resistivity and Seebeck coefficient at 100-200°C were measured on all elements. The n-PbTe samples generally conformed to within ten percent of the values published by 3M. Tests on the p-PbSnTe were less satisfactory. Resistivity results were somewhat erratic but generally fell within ten percent of the value reported by 3M for the lot of powder supplied. Seebeck coefficients in the earlier specimens were again erratic, but most were within ten percent of the published 3M values. Tests of more recent production yielded results consistently below the 3M values, the most recent samples being about 40 percent below predicted.

There has been no discernable change in procedure during this period leading to the tentative conclusion that the powder was inhomogeneous or has become contaminated by absorbing oxygen or other gases from the atmosphere. Metallographic examination of samples indicated no difference in appearance as a function of time. Two elements, one pressed early in the program and the other produced recently, have been delivered to GSFC for analysis by the electron microprobe technique. If any difference in dopants or impurities can be detected they will help to explain our anomalous results.

IV. BRAZE PROCESS DEVELOPMENT

Approximately fifty bonding tests have been conducted during the quarter, almost all employing the basic joining process developed for p- and n-PbTe during the first phase of this program. Work has also progressed on a tin soldering process for attaching cold shoes to thermoelectric elements.

The process for brazing iron hot shoes to PbTe and PbSnTe with SnTe - 1 w/o Ti braze ~~are~~ is described below. The materials are prepared as follows:

1. Iron Shoes: The machined shoe is polished successively on 400 and 600 grit paper and then finished on polishing wheels with No. 3 universal diamond paste followed by 1 micron alumina. The shoe is then scrubbed in hot soapy water, rinsed in clear water, wiped with acetone, rinsed with methanol and stored in methanol until used.

2. p-PbSnTe: Hot pressed p-type elements normally have small chips missing at the corners. The elements are ground flat on 180 grit paper until a complete circular cross section is achieved. Almost 1/16 inch is usually removed from each end. Following this operation the procedure is identical to that used with the shoe materials.

3. n-PbTe: About 1/32 inch is ground from each end of the elements. Parallel score marks are then made by drawing the elements in one direction across 180 grit paper. The elements are then cleaned in soapy water, rinsed with water, wiped with acetone, rinsed with methanol and stored in methanol.

4. Braze Wafers: High purity tin, tellurium and titanium are weighed out in the correct proportions and melted under a partial pressure of high purity argon. The melt is crushed into powder, blended, pressed into 3/8 inch diameter by 0.010 inch thick wafers and sintered under purified argon for 3 hours at 540°C. The wafers are then stored in methanol.

Elements are bonded in the following manner. The shoes, element and braze wafers are removed from the methanol in which they are stored and dried with clean Kimwipes. The components are assembled and placed in a graphite alignment sleeve which is in turn inserted into the steel brazing jig. Light pressure is applied through a spring to hold the assembly in position. The assembly is inserted into a large vycor tube which is sealed, evacuated and purged with argon. A small argon flow is maintained. The vycor tube is inserted into a furnace. The temperature is raised to 800° - 815°C, held for five minutes and allowed to furnace cool to about 600°C.

The assembly is then placed into a brick holding chamber which allows it to slowly cool to 200°C at which time it is opened and the assembly removed.

This process continues to produce satisfactory n-PbTe elements. Consistent, satisfactory bonds of p-PbSnTe to iron have not been produced. Rigid adherence to the sample preparation procedure is necessary for bonding to occur. Weak bonds that separated during handling have resulted from minor deviations from the cleaning process.

In those instances where strong bonds were obtained cracking frequently occurred in the PbSnTe adjacent to the bond as a result of thermal stresses during cooling. This is not unexpected since such a possibility was discussed in the thermal stress analysis of Reference 1 and since 3M reports that p-PbSnTe is weaker than the p-PbTe material. This problem may be approached by (1) increasing the strength of the thermoelectric material, (2) selecting another shoe material with thermal expansion coefficient closer to that of PbSnTe, or (3) increasing the ductility of the braze material. Development is continuing with emphasis on the first two approaches.